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Recent Development of Surface Modification Processing

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1. Introduction

Recently precision machines and tools are required to be highly precise, functional and long lasting, and they are used under severe conditions such as high vacuum, high temperature, highly corrosive environment. In order to respond to these severe demands, developments of surface modification techniques are increasingly urged, and actually various new techniques are proposed. The Society of Precision Engineering in Japan established a subcommittee for Investigation and Research on Surface Modification in 19[illegible]6. The committee is still investigating recent surface modification technologies, especially dry process. In November [illegible] the committee held a symposium on "New Surface Modification Technology and Tribology", and now the committee is preparing a monograph, "Surface Modification", to be published from Nikkan Kogyo Shinbunsha.

In this special issue frontier scientists review various aspects of surface modification, particularly film formation processes of superhard films such as diamond and cBN. If these films are applied to practical use, their effects on materials industries are enormous. Though the development of new technology is sought all over the world, no practical techniques have been established yet. The main purpose of this special issue is to present characteristics of various film formation techniques and to induce new ideas.

In this article, we review (overall) characteristics of various dry processings, their applicable area, and problems. Further, we present recent developments and problems of superhard films as an introduction to this issue.

2. Current Status of Surface Modification Technology

Recent surface modification technology may be classified into coating methods such as CVD (chemical vapor deposition) and PVD (physical vapor deposition)

and formation of surface layers such as surface diffusion or surface structure regulation. Energy sources for surface modification are traditionally heat (electrical furnace, high frequency heating, plasma heating etc.), but now ions, EB (electron beam) and laser are new energy sources. Table I lists principles and characteristics of various techniques. In this Table "Yosha" represents deposition of melting particles, which, strictly speaking, is not PVD. However, it is included in PVD since its treatment is very similar to PVD. Diffusion treatment using laser and EB is a phenomenon of phase mixing on the surface melting layer. Grafting and ceramic formation, which form different materials on the surface, do not belong to diffusion treatment but again we classified them in the diffusion treatment column since those treatments are very similar to diffusion treatment.

History and current applicationsare in the order of heat, ion, EB, and laser. Though lasers have great potential, their practical applications are few. The laser CVD (exima laser) and laser PVD (mainly CO_2 laser) are new film making methods using non-thermal photo chemical reactions and evaporation phenomena of high melting point materials. 1504

EB is quite old in the vapor deposition method. With development of controlling beams, EB is considered to be effective to fine shapes.

Ion is a central technique of all surface modification techniques and it becomes a main technique of the dry processing. It can activate various reaction agents, process at lower temperatures, and promote reactions. Thus, this plays an important role in makinghighly functional surfaces. There are a number of PVD using ions. For example, practical applications of the ion plating method are summarized in Table 2.[4] The ion sputtering method involves DC2K, RF2K, perpendicular electromagnetic fields (magnetron, hollowcathode, etc.), and facing

Table 1 Principles and Characteristics of Dry Process Surface Modification

Method	Modified Film		Modified Layer	
	CVD	PVD	Diffusion	Structure Controlling
laser	chemical reaction (photo chemistry, thermal decomposition)	evaporation Yosha	alloys, ceramics, grafting	quenching, annealing, amorphous, melt hardening, magnetic control
electron beam (EB)		evaporation	alloys grafting	quenching, annealing, amorphous, melt hardening, polymerization, decomposition
ion	activating reaction species, low temperature	activating reactants, sputtering, accelerating plating		injection, mixing
[illegible]	thermal reaction	Yosha	Shitan, nitrogezation, calorizing	quenching

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Table 2 Classification of Ion Plating

	classification
	direct current ion plating method
plasma method	high frequency current ion plating method
(low vacuum)	holo cathode method
	ARE method
	high frequency ion plating method
	arch discharge type
ion beam method	cluster ion beam method
(high vacuum)	electron shower method
	ion beam epitaxy method

[illegible] types. Even in the superhard film processing which is a main subject in this issue ions are effectively used.

Surface modification using heat has been widely utilized as a thermal treatment, and thermal CVD and "Yosha" are most practical techniques.

Correlations between function and technique required for surface modification are classified in Table [illegible]. In this Table we mainly focus on machine and tool parts and exclude applications to electronics and optelectronics. From this Table surface modification applies most to wear resistance parts, and then lubricating, anticorrosiveness, and heat resistance.

The main objective of surface modification is to add highly functional technology to small part of inexpensive materials. From now on more and more higher

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Table [illegible] Relation between Surface Modification Method and Required Functions and Their Usages

method	CVD	PVD	Diff*	Str**	Usage
wear resistance	○	○	○	○	piston ring, mold, roll, artificial joint, lens protection, bearing, tool, rotary engine parts, pulley, wrinkling parts, disc protection, shaft, valve, gear housing, nozzle, blade
lubrication		○	○	△	bearing, magnetic disc, artificial joint, wrinkling parts
anti-corrosion	○	○	○		turbine blade, boiler, arc welding electrode, heat exchanger, nozzle
heat resistance	○	○	○		turbine blade, nuclear fusion furnace wall, arc welding, industrial furnace wall
optics	○	○			reflecting mirror, glasses, lens, absorption body, decoration
insulation	○	○		○	insulation film, wire coating
magnetism				○	magnetic iron board
[illegible]	○	○			speaker vibrating board
human body		○		△	artificial joint, artificial bone, artificial tooth root

* diffusion ** structure control

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technologies and wider applications will be sought. We lists current problems concerned with surface modification technology

For surface modifications such as CVD and PVD

(1) increasing the vapor deposition rate,

(2) improving adhesivity to the base board,

(3) homogeneity of film composition and thickness (both parallel and perpendicular to the surface),

(4) application to complex shapes (homogeneity, adhesivity)

For surface modifications such as diffusion and structure control

(1) optimizing the diffusion condition,

(2) controlling shapes of treated surface,

(3) improving absorption of supplied energy.

3. Recent Development of Superhard Thin Film Technology /305

Though the discovery of high temperature superconductive materials surpassed the superhard thin film technology, the thin film formation technique of superhard materials such as diamonds and cBN is of most attention in the surface modification technologies. The methods of forming superhard thin films are listed in Table 5. Some of them are semi practical, but industrial applications have not been attained. By the year 2,000, total industrial sales in the diamond market are estimated to be about $100 billion.

Diamond is very hard, has superior electrical resistance and thermal conductivity, and thus can widely be utilized. Tool makers are trying to develop diamond thin film bite. Recently, a thin film tool was made by the electron activation chemical vapor deposition method. It was reported that the tool worked great

cutting aluminum alloys. Besides tools, wear resistance surfaces, wear resistant wrinkling planes, and rollers will use diamond films, which were considered expensive previously. Diamond has excellent properties for electronics and its usage in electronics will be increasing over wear resistance usage. Table 4[2] lists various applications as electronics materials. Most promising applications will be thin film semiconductors which use superior properties of diamonds such as large band gap, low dielectric constant, good thermal conductivity.

cBN also has similar properties to diamonds and its thin films are as important as diamond. Diamond is mainly applied to non-iron materials while cBN is more suitable for iron materials. Thus, for application to tools cBN may be more valuable than diamond. However, the filming technology of cBN is behind that of diamond. Thus, before applications to coating tools which must endure severe mechanical and thermal conditions, other applications, which utilize chemical stability, high temperature resistance, anticorrosiveness, wear resistance, and electrical high functions of CBN, will be realized.

Several methods of making diamond and cBN films are listed in Table 5. Diamond films which have crystal structures close to natural bulk diamonds are made by the CVD method. The basic mechanism of diamond synthesis by the CVD method is that hydrocarbons consisting mainly of methane (CH_4) are diluted by H_2 gas, heated to about 1,500°C, activated and decomposed. In other words, the methyl radical CH_3 is essential to synthesizing diamonds, and activated hydrogen molecules pull H from methane to form methyl radicals. Further hydrogen gas reacts with graphite layers coexisting with diamonds and makes graphites gaseous.

The present status of CVD method for synthesizing diamond films is as follows:

Table 1 Usages of Diamond Electron Materials

Property	Application	Characteristics
insulation	surface protection film	resistance to high voltage (> 10[illegible] V/cm)
thermal conductivity	base board, heat sink	highly thermally conductive base board, high power laser
transparency	transparent window to visible and ultrared light, laser ends protection	life, reliability, wide wave length ranges
sound velocity	speaker material, ultra sound transmission media	wide ranges
low friction coefficient	surface coating, disc surface	wear resistance, lubrication
semiconductivity	transistor, FET, ultra high temperature motion Tr (wide gap), photo electron motive force element, ultraviolet sensor	radiation resistance, high speed motion 500°C, high speed optical switch
anti-ion barrier	passivation, surface protection film	Na ion prohibition

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Table 3-1 Diamond cBN Thin Film Synthesis.

	CVD method		
	synthesis	basic process	formed film
	hot filament	CH_4, C_2H[illegible], C_2H_2 – H_2	D
		alcohol, acetone – H_2	D
D	direct current plasma	CH_4 – H_2	D, a-C
I	high frequency plasma	CH_4 – H_2	D, G
A	microwave plasma	CH_4 – H_2	D
M	high frequency thermal plasma	CH_4 – H_2 – Ar	D
O	ECR plasma	CH_4 – H_2	D
T	electron beam irradiation CVD	CH_4 – H_2	D
D	ArF laser CVD	C_2H_2 – H_2	D
		C_2H_5Cl – H_2 – Ar	a-C
	vacuum ultraviolet light – EB gun	CH_4 – H_2	D
[illegible]	reactive pulse plasma	B_2H_6 – N_2 – H_2	cBN, wBN
D	plasma-chemical transport	B – N_2 – H_2	cBN, wBN
N	thermal electron radiation of plasma	B_2H_6 – NH_3 – H_2	cBN
	ECR plasma	B_2H_6 – N_2, acceleration	cBN

Table 3-2 Diamond cBN Thin Film Synthesis.

	PVD method		
	synthesis	basic process	formed film
	ion beam sputt	$Ar + H_2$ ion G sputt	D, a-C
	CO_2 laser sputt	G sputt by $10^{[illegible]}$ W/cm^2	a-C
D	ion sputt + ion gun	C sputt + H^+ acceleration	D
I	ion plating	G evaporation + H_2 ionization, acceleration	D
A	anion beam deposition	C^-, C_2^- acceleration	a-C
M	ICB	C_2H_2 thermal electron ionization, acceleration	a-C
O	inonization depositon	CH_4, C_2H_2 inonization, acceleration	D, a-C
N		C_xH_y + Ar ionization, acceleration	a-C
D	high frequency ion plating	$CH_4 + H_2$ ionization, acceleration	a-C
	double plasma	CH_4 ionization, acceleration	a-C
	HCD-ARE	B evaporation + N_2 ionization, acceleration	cBN
c	EB ARE	B evaporation + N_2 ionization, acceleration	cBN
B	IVD	B evaporation + N_2 ionization, acceleration	cBN
N	ionization vapor deposition	B evaporation + N_2 ionization, acceleration	cBN
	CO_2 laser PVD	hBN evaporation	aBN
		hBN evaporation + N_2 ionization, acceleration	cBN
	ion beam	$B_3N_3H_6$ ionization, acceleration	cBN, wBN

D: diamond, G: graphite, a-C: amorphous hard carbon, wBN: wurtz type BN,
aBN: amorphous hard BN

(1) Instead of hydrocarbons, organic compounds such as alcohols and acetone are used, since they produce more methyl radicals than hydrocarbons. The rate of film formation is increased by activating under a high temperature environment such as thermal plasma.

(2) In order to make uniform and smooth films by densely generating nuclei, the base board and synthesizing method are developed.

(3) To relax internal stresses during synthesis and to increase adhesiveness, the base board material, temperature, and reaction conditions are optimized.

The PVD method is to collide high speed ions and gas particles with the base board. This method yields amorphous carbons contrary to film synthesis by the CVD method. By sputtering of graphites, ionization of hydrocarbons and acceleration of them by bias potential, superhard carbon films are synthesized. However, they are mostly amorphous. Ionization and acceleration of the latter yield amorphous carbon films, which are usually called i-C. However, we classified them in [illegible]. There are a couple of advantages using the PVD method: the base board temperature can be low (less than several hundred °C), large films may be obtained, the film surface is smooth and can be used without reabrasion. The current problems associated to this method are that the rate of film formation is slow, film compositions and structures are unstable, and the resulting films weakly adhere.

For cBN, both CVD and PVD methods are developed. Contrary to diamond synthesis mentioned above, the PVD method is ahead of CVD. An EB gun makes evaporates metal B, or CO_2 laser has hBN evaporates and simultaneously irradiation and bias acceleration of ionized N attains cBN. Some methods yield wBN (wurtzite type Boron nitrate) which is intermediate between cBN and hBN.

The problems associated with cBN film synthesis are as follows:

(1) It is difficult to control B/N ratio as close as the stoichiometric value. Very often B rich films are formed.

(2) In diamond synthesis, unwanted graphites coexist. Similarly, for cBN film formation, hBN can not be excluded.

(3) BN itself is chemically stable and thus adhesiveness of BN to the base board is not strong.

It will take some time before coating tools which are expected to work for iron materials becomes practical.

4. Conclusion

We discussed surface modification technologies, of which the dry process is most important, and reviewed superhard thin film synthesis. In 1970, diamond films were synthesized in the USSR. Since then with this as a turning point research and development have been initiated in Japan in 1980's. The Japanese research level is one of the highest in the world. Various techniques presented in this issue are unique and their future will be promising. This article is written following our activities in the committee.

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15. Supplementary Notes

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16. Abstract

A review with 4 refs. is given on the formation of superhard thin films, e.g., diamond, cubic BN, by dry processes (e.g., chem. vapor deposition, phys. vapor deposition, diffusion).

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